SPECTROSCOPIC METHODS

UNIT - I

Term Symbols

- **Term Symbol Form: $^{2S+1}\{L\}_J$**

- 2S+1 – multiplicity
- L – resultant angular momentum quantum number
- J – total angular momentum quantum number

- Ground state has maximal S and L values.

- Example: Ground State of Sodium – $1s^2 2s^2 2p^6 3s^1$
- Consider only the one valence electron ($3s^1$)
- L = l = 0,
- S = s = ½,
- J = L + S = ½
- so, the term symbol is $^2S_{½}$

Derivation of P^2 Configuration

- C – $1s^2 2s^2 2p^2$
- Step 1:Consider two valence p electrons
- 1^{st} 2p electron has n = 2, l = 1, m_l = 0, ±1, m_s = ±½ → 6 possible sets of quantum numbers
- 2^{nd} 2p electron has 5 possible sets of quantum numbers (Pauli Exclusion Principle)
- For both electrons, (6x5)/2 = 15 possible assignments since the electrons are indistinguishable
- Step 2: Draw all possible microstates. Calculate M_L and M_S for each state.

All Possible Microstates

	m_l				
	+1	0	−1	M_L	M_S
	↑	↑		1	1
all up	↑		↑	0	1
		↑	↑	−1	1
	↓	↓		1	−1
all down	↓		↓	0	−1
		↓	↓	−1	−1
	↑↓			2	0
	↑	↓		1	0
	↑		↓	0	0
one up	↓	↑		1	0
one down		↑↓		0	0
		↑	↓	−1	0
	↓		↑	0	0
		↓	↑	−1	0
			↑↓	−2	0

Step 3: Count the number of microstates for each M_L—M_S possible combination

Step 4: Extract smaller tables representing each possible term

table

		M_S		
		+1	**0**	**−1**
	+2		1	
	+1	1	2	1
M_L	**0**	1	3	1
	−1	1	2	1
	−2		1	

S=0, L=2, J=2

$^1D_2$

		M_s
		0
	+2	1
	+1	1
M_l	**0**	1
	−1	1
	−2	1

S=1, L=1, J=2,1,0

$^3P_2$, $^3P_1$, $^3P_0$

		M_s		
		+1	**0**	**−1**
	+1	1	1	1
M_l	**0**	1	1	1
	−1	1	1	1

S=0, L=0, J=0

$^1S_0$

		M_s
		0
M_l	**0**	1

Step 5: Use Hund's Rules to determine the relative energies of all possible states.

- 1. The highest multiplicity term within a configuration is of lowest energy.
- 2. For terms of the same multiplicity, the highest L value has the lowest energy (D < P < S).
- 3. For subshells that are less than half-filled, the minimum J-value state is of lower energy than higher J-value states.
- 4. For subshells that are more than half-filled, the state of maximum J-value is the lowest energy.
- Based on these rules, the ground electronic configuration for carbon has the following energy order:
- $^3P_0 < {}^3P_1 < {}^3P_2 < {}^1D_2 < {}^1S_0$

L	Symbol	S	Multiplicity (2S+1)	J	Symbol
2	D	0	1	2	$^1D_2$
1	P	1	3	2,1,0	$^3P_2$, $^3P_1$, $^3P_0$
0	S	0	1	0	$^1S_0$

Partially filled orbitals have two perturbations

- Inter Electronic Repulsions
- Spin – Orbit coupling

Inter – Electronic Repulsions

- Energy depends on the arrangement of electron
- The electrons in partially filled orbitals repel each other.
- Repulsion splits the energy levels resulting in many terms.
- Energies of electrons within an orbital itself are slightly different (Pairing and Exchange energies).

Racah Parameterrs (A, B and C)

- Racah parameters were generated as a means to describe the effects of electron – electron repulsion within the metal complexes.
- A is ignored because it is roughly the same for any metal center.
- B is generally approximated as being 4C
- B represents is an approximation of the bond strength between the ligand and metal.
- Comparisons between tabulated free ion B and B’ of a coordination complex is called nephelauxetic ratio (the effect of reducing electron – electron repulsion via ligands).
- This effect is what gives rise to the nephelauxetic series of ligands.

Nephelauxetic Effect

- Normally the electron repulsion is found to be weaker in complexes than in free ion and this means the value of B for the complex less than for a free ion.
- This is due to the delocalization of the electron over the ligands away from the metal which separates them and hence reduces repulsion.
- The reduction of B from its free ion is normally reported in terms of nephelauxetic effect

$$\beta = \frac{B' \text{ complex}}{B \text{ free ion}}$$

- **Where β is the nephelauxetic parameter and refer to the electron cloud expansion.**

Nephelauxetic Series

- The value of β depend on the ligand and vary along the nephelauxetic series. The ligands can be arranged in a nephelauxetic series as shown below. This is the order of the ligands ability to cause d electron cloud expansion.

$$\mathbf{I^- < Br^- < Cl^- < CN^- < NH_3 < H_2O < F^-}$$

- The series tell us that a small value of β means that there is large measure of d – electron delocalization and a greater covalent character in the complex.

Reasons for e^- cloud Expansion

- The electron cloud expansion effect may occur for one (or both) of two reasons.

1. One is that the effect positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the d – orbitals can expand slightly.

2. The second is the act of overlapping with ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals.

Spin – Orbit Coupling / L – S Coupling / RS Coupling

- Responsible for fine structure of spectrum.
- Electron has both spin and orbit angular moment and associated magnetic moments.
- These magnetic moments interact weakly to split the energy levels.

Russel – Saunders for light atoms

- Couple all individual orbital angular momenta l to give a resultant total orbital angular momentum L.

$$\mathbf{L = \Sigma l_j}$$

- Couple all individual spin angular momenta s to give a resultant total spin angular momentum S.

$$\mathbf{S = \Sigma s_j}$$

$$J = L + S, L + S - 1, \ldots, |L - S|$$

$$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$

$$S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2|$$

j – j Coupling

- Couple individual orbital l and spin s angular momenta first to the complete electron angular momentum j.

$$j = l + s$$

- Couple all f to give the total angular momentum J

- j-j coupling is much more complicated to treat, but should be used for elements heavier than bromine.

- For 4d and 5d series of ions.

Orgel Diagram

- Used for interpretation of electronic spectra of metal ion complexes.
- Got by plotting the energies of split levels of a term by increasing ligand field strength.
- **Only applicable for weak field cases.**
- **Can predict only spin – allowed transition.**
- Transition are assumed to occur from the lowest energy level.